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RESEARCH HIGHLIGHTS

• A new hetero-bimetallic Zn(II)/Ca(II) complex was synthesized using hexadentate

N₂O₄ proligand

- X-ray single-crystal structure of complex was determined
- Fluorescence and DFT/M06 investigations were performed
- Antibacterial efficacy, solvent effect and bacterial killing efficiency were examined
- A docking study with DNA Gyrase and DNA Polymerase III proteins corroborate the

experimental findings

A rare hetero-bimetallic Zn(II)/Ca(II) Schiff base complex: Synthesis, crystal structure, DFT, molecular docking and unveiling antimicrobial activity

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ABSTRACT

A new hetero-bimetallic Zn(II)/Ca(II) complex, $[Zn_2(L^{OMe-pn})_2(\eta^1-NCS)_2Ca]$ (1) has been synthesized using a potentially hexadentate N_2O_4 proligand, $H_2L^{OMe-pn} = N,N-bis(3$ methoxysalicylidene)-2,2-dimethylpropane-1,3 diamine and structurally well characterized by different physicochemical techniques. Single crystal X-ray diffraction study of the complex revealed that, de-protonic form of the ligand utilizes two pockets, one is occupied by Zn(II) ion and other is housed by a Ca(II) ion. The Zn centres are fitted into the N_2O_2 compartment with distorted square pyramidal geometry while a large open O2O2' compartment is occupied by a Ca(II) ion in a octacoordinated environment. DFT studies were successfully carried out using DFT/M06 functional level and 6-31G * basis set (over all the atoms) to delineate the complex optimized structure, composition of the frontier molecular orbitals, global reactivity, total energy frameworks, MEP, total dipole moment, average polarizability and first hyperpolarizability. First hyperpolarizability value (59.62 x 10⁻³¹ esu) suggests that complex is a good NLO material. Hirshfeld surface revealed the presence of many short intermolecular contacts like C···H/S···H/N···H/O···H/H···H/C···C and S···S in the crystal structure. The experimental absorption spectra are comparable with the electronic transitions assigned from TD-DFT studies. CHEF based $(\pi \rightarrow \pi^*)$ luminescence property has been measured in DMSO solvent at room temperature. Concentration dependent antibacterial efficacy was investigated against gram-negative bacterial strains viz. Escherichia coli (ATCC 25922) & Pseudomonas aeruginosa (ATCC 27853) and gram-positive bacterial strains viz. Staphylococcus aureus (ATCC 25923) & Bacillus subtilis (ATCC 6633). The bacterial killing efficiency and solvent effect of the complex was compared with that of ligand. Finally, a docking study with the active site of DNA Gyrase and DNA Polymerase III proteins has been carried out to corroborate the experimental findings.

Keywords: Antibacterial, Schiff base, Zn(II)/Ca(II), DFT, Fluorescence, Molecular docking

1. Introduction

In recent years, the design and syntheses of hetero-bimetallic complexes using salen-type ligands are continuously pledging immense interest due to their diverse field of applications in coordination chemistry [1-16]. Complexation with the introduction of another new metal centre may possibly change the topologies and the coordination environments which largely affect various physicochemical properties like magnetic, catalytic, Photoluminescent etc. Such classified heteronuclear complexes have been synthesized using bicompartmental N/Odonor Schiff bases which are commonly derived from salicylaldehyde derivatives ortho vanillin and usual diamines [17]. Curiously, Calcium is the fifth most abundant element in the Earth's crust, and the third most abundant metal, still coordination chemistry of Ca(II)-Schiff base is rare. The beginning of Calcium-Schiff base complexes started from 1977 by Bullock and Tajmir-Riahi in relationship with trivalent lanthanides. Very few instances of Ca(II)-MOFs or N/O-donor complexes are explored within the literature which are excellent luminescent under UV/Vis excitation [18]. The ring-opening polymerization, hydrogenation, hydroboration, hydroamination, hydrosilylation and amine-borane dehydro-coupling are other significant uses of novel Ca(II) buildings [19]. The stereochemical condition of Ca(II) buildings is amazing, it ought to be either hexa or octa coordinated. Furthermore, polydentate phenol-based ligands possessing unique bicompartmental nature, because of its ability to provide two adjacent coordination sites with dissimilar environment functioning as binucleating agent [20]. Single crystal X-ray diffraction study diagnoses the mode of encapsulation of the metal (M^{2+}) ions in the ligand proximity without exception [21-25]. Apart from conventional homonuclear complexes, our recent research focus has been on heterometallic complexes [26-28] due to their multifaceted synthetic advantage. In this context crown ethers/cryptands are another important class of complexing agent for s-block

or 3d series metal ions [21] but hexadentate N_2O_4 proligand is effectively bound to sblock/3d/4f metal ions [21,29-37]. Such labile ligands played not only an important role in the development of coordination chemistry [38] but also their significant contribution in the development of inorganic biochemistry [39], catalysis [40], electrochemical conduction [41,42], ion recognition [43-46], supramolecular architectures [47,48], magnetism [49,50], optical devices [51] and luminescent materials [52-55]. Moreover, homo/heteronuclear Schiff base complexes have been attracting much attention in the curated area due to awesome ligating behaviour and have a wide spectrum of biological applications, e.g., DNA binding [56], antimicrobial [57], anticancer [58,59], antitubercular, antiangionesis [60,61], antiviral [62], antipyretic [63], antiparasitic, anti-inflammatory [64], anti-HIV and anti-convulsant [65]. These biological applications are greatly influenced by the structural diversity of the complex, the presence of azomethine linkage as well as the substituents bound on the Schiff base ligands [66]. Remarkably, computer aided drug design (molecular docking) of Schiff base complexes are another recent development in biological coordination chemistry [67]. Today DFT in conjunction with molecular docking analysis is inevitable to explore several molecular interactions between the synthesized metal complex and proteins [67]. Thiocyanate [SCN] ion is a versatile pseudo-halide that can coordinate to metal ions in an assortment of bridging modes (Scheme S2). Along these lines, hexadentate N₂O₄ proligand in association with pseudo-halide ions have been utilized over many years for the synthesis of homo/heterometallic complexes [68,69] which show interesting structure and molecular topologies, where the molecular architecture is governed not only by the nature of pseudohalides but also depends on the steric requirements of the ligands [70]. The chemistry of group 12 metal ions has always exhibited flexible geometry due to their d¹⁰ configuration and zero crystal field stabilization energy (CFSE) [71]. The selection of biologically important Zn²⁺ metal ion is not only based on the novel applications of emitting materials for organic

light emitting diodes [72], but also due to the fluorescent sensors for organic/inorganic analyses [73]. In the last few years, we have explored Group 12 metal ions coordination behaviour with compartmental salen-type ligands and their photoluminescence, DFT/TD-DFT, molecular docking, cytotoxic effect, autophagy, apoptosis/necrosis type classical cell death, *in vitro* antibacterial and anti-biofilm properties vividly [74-78]. The result is the consistent of photoluminescence, cytotoxicity, antibacterial and anti-biofilm properties yet it is noteworthy that no exiguous number of research works have been devoted in favour of hetero-nuclear complex formation with hexadentate N_2O_4 proligand and pseudo-halide [SCN⁻] spacers. In spite of the fact that the broad literature survey investigates chemistry of discrete/di/trinuclear 3d/alkali metal/salicylaldimine complexes [79] but exceptionally few looks into their structures [80,81] and novel properties.

In this paper, we have reported the synthetic details, spectral characterizations, X-ray crystal structure, DFT investigations, along with concentration dependent antibacterial efficacy and fluorescence studies of complex **1** in the presence of a potentially hexadentate N_2O_4 proligand, (H₂L^{OMe-pn}). Subsequently, molecular docking studies were performed in order to understand the binding capability of the complex with active site of DNA Gyrase and DNA Polymerase III proteins.

2. Experimental section

2.1. Materials and physical measurements

All chemicals were of analytical reagent grade and used as received without any purification. Zn(OAc)₂.2H₂O, Ca(SCN)₂.4H₂O, *ortho* vanillin and 2, 2-dimethyl-1,3-propanediamine were purchased from Sigma Aldrich Company, USA. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. FT-IR and Raman spectra were recorded as KBr pellets (4000–400 cm⁻¹) using Perkin–Elmer spectrum RX 1 and BRUKER RFS 27 (4000-50 cm⁻¹). ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz and 75.45

MHz FT-NMR spectrometer using trimethyl silane as internal standard in DMSO-d₆ solvent. EDAX and SEM experiments were performed on EDAX OXFORD XMX N Model using Tungsten filament and JEOL Model JSM - 6390LV. UV-Vis spectra (200-1100 nm) were determined using Hitachi model U-3501 spectrophotometer. Fluorescence spectra in DMSO solvent were measured at room temperature using Perkin-Elmer LS50B Spectrofluorometer model. Powder X-ray diffraction measurements were carried out by BRUKER AXS, GERMANY X-ray diffractometer D8 FOCUS model using Cu K α -1 radiation. Quantum yield (Φ_F) of compounds was determined using equation (1) with reference to quinine sulfate as a secondary standard ($\Phi_F = 0.57$ in water) [82].

$$\frac{\Phi_s}{\Phi_R} = \frac{A_s}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{n_s^2}{n_R^2}$$
(1)

According to equation (1): A terms denote the fluorescence area under the curve; Abs denotes absorbance; n is the refractive index of the medium; Φ is the fluorescence quantum yield; and subscripts S and R denote for the studied sample and reference respectively.

2.2. X-ray crystallography

Crystals of complex **1** were grown by slow evaporation of CH₃OH-DMF solvent medium at room temperature. Good quality crystals data were collected on a Bruker *SMART* CCD [83] diffractometer using Mo K_a radiation ($\lambda = 0.71073$ Å) at 140 K. Judicious crystal data collection purpose, we have utilized different common programs such as *SMART* for collecting frames of data, indexing reflections and determining lattice parameters, *SAINT* [84] for integration of the intensity of reflections and scaling, *SADAB* [85] for absorption correction and SHELXTL for space group, structure determination and least-squares refinements on F^2 . Crystal structure was fully solved after refining by full-matrix leastsquares methods against F^2 using *SHELXL-2014* [86] and *Olex-2* software [87]. Further, all the non-hydrogen atoms were refined with anisotropic displacement parameters and all

hydrogen positions were fixed at calculated positions which are refined iso-tropically. All crystallographic figures were designed using Diamond Version 4.6.3. The crystallographic data and full structure refinement parameters for complex **1** are clearly submitted in Table **1**.

Formula	$C_{44}H_{48}CaN_6O_8S_2Zn_2$		
M/g	1023.82		
Crystal system	Monoclinic		
Space group	$P2_1/c$		
a/Å	24.363(2)		
b/Å	19.4085(9)		
$c/{ m \AA}$	19.8148(17)		
β (°)	93.881(3)		
$V/Å^3$	9348.0(15)		
Z	8		
$\rho_{c}/\mathrm{g~cm}^{-3}$	1.455		
μ/mm^{-1}	1.283		
F(000)	4240		
Cryst size (mm ³)	$0.26 \times 0.22 \times 0.20$		
θ range (deg)	2.26 to 25.00		
Limiting indices	$-28 \le h \le 28$		
	$-23 \le k \le 23$		
	-23≤1≤23		
Reflns collected	181406		
Ind refins	$16429[R_{\text{int}} = 0.1769, R_{\text{sigma}} = 0.0931]$		
Completeness to θ (%)	0.999		
Refinement method	Full-matrix-block least-squares on F ²		
Data/restraints/ parameters	16429/0/1145		
Goodness-of-fit on F^2	1.070		
Final <i>R</i> indices	$R_1 = 0.0721$		
$[I > 2\theta(I)]$	$wR_2 = 0.1198$		
R indices (all data)	$R_1 = 0.1366$		
	$wR_2 = 0.1415$		
Largest diff. peak and hole ($e \cdot \text{Å}^{-3}$)	1.08 and -0.65		

Table 1 Crystal data and full structure refinement parameters for complex

2.3. Computational methods

Complex geometry optimization was carried out using Gaussian 16 programming package [88]. All geometries in DMSO (Dimethyl Sulfoxide) have been optimized and the solvent effect was estimated with the polarized continuum model (PCM) [88]. For complete DFT calculations, the new highly parameterized approximate exchange-correlation energy functional M06 (Meta-generalized gradient approximation (GGA) functional exchange) was selected [89,90]. Calculations were performed using a valence double-zeta polarized basis set 6-31G* over all the atoms. Considering the presence of a minima of the potential surface, the vibrational analysis was carried out which revealed a lack of imaginary frequencies. The time-dependent density functional theory (TD-DFT) was employed for complex 1 at M06/6-31G* functional level of theory in DMSO using PCM model to obtain an insight into the participation of various frontier molecular orbitals (FMOs) and their related contribution to the UV-Vis absorption spectrum. These calculations were performed after geometry optimization at ground electronic state to obtain vertical electronic transition energies. The Gauss View 6 program was used to visualize the optimized structures, molecular electrostatic potential (MEP) plot, graphics of the frontier molecular orbitals and theoretically calculated UV-Vis spectra [91]. Gauss sum [92] was used in the final phase of the theoretical computation to calculate the fractional contribution to each molecular orbital of the various individual elements existing in the complex. The theoretical calculation of the first hyperpolarizability (β^{hyp}) and its component using finite field (FF) approach was carried out at M06/6-31G* level of theory. For calculation of first hyperpolarizability (β^{hyp}) of a variety of chemical systems, the FF approach has been used which provide very constant results in accordance with the experimental results [93]. The total static dipole moment was calculated using equation (1) as

$$\mu = \mu_x^2 + \mu_y^2 + \mu_z^2 \tag{1}$$

The isotropic polarizability was calculated using equation (2) as:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

(2)

The first-order hyperpolarizability (β^{hyp}) was calculated using equation (3) as:

$$\beta^{\text{hyp}} = \left[\left(\beta^{\text{hyp}}_{xxx} + \beta^{\text{hyp}}_{xyy} + \beta^{\text{hyp}}_{xzz} \right)^2 + \left(\beta^{\text{hyp}}_{yyy} + \beta^{\text{hyp}}_{yzz} + \beta^{\text{hyp}}_{yxx} \right)^2 + \left(\beta^{\text{hyp}}_{zzz} + \beta^{\text{hyp}}_{zxx} + \beta^{\text{hyp}}_{zyy} \right)^2 \right]^{\frac{1}{2}}$$
(3)

2.4. Antibacterial assay

The antimicrobial efficiency of complex (C1) was investigated comparatively with ligand (L1) against gram-negative bacterial strains viz. Escherichia coli (ATCC 25922) & Pseudomonas aeruginosa (ATCC 27853) and gram-positive bacterial strains viz. Staphylococcus aureus (ATCC 25923) & Bacillus subtilis (ATCC 6633). The antibacterial activity was investigated through concentration dependent bacterial growth inhibition assay using micro-dilution method [94] in 96 well plate. Briefly, all bacterial suspension was cultured in Luria Bertini (LB) broth in 96 well plate. Complex and ligand at different concentrations (5, 10, 25, 50, 100, 200, 500, 700, 1000 µM) were added in respective well containing a bacterial culture and incubated for 24 h in mild shaking condition at 37°C.The bacterial growth inhibition was evaluated by recording the optical density (O.D) at 600 nm using microplate reader (Biorad, USA) compared to control. Herein, standard antibiotic solution (aqueous) gentamicin sulphate (10 µg/mL) was utilized as a positive control. As the complex and ligand were soluble in dimethyl sulfoxide (DMSO) and methanol (CH₃OH) respectively, the solvent effect on bacterial growth [95] has also been investigated. The bacterial cells viability was presented as percentage of relative survival. Cell viability was determined using the following equation,

$$Cell \, Viability(\%) = \frac{OD_{Sample} - OD_{Blank}}{OD_{Control} - OD_{Blank}} \times 100$$

The absorbance values of treated cells and untreated cells are denoted as OD_{Sample} and $OD_{Control}$ respectively. The whole assay was performed with independent triplicate experimental setup to obtain the standard mean values. Further, the killing efficiency of complex and ligand were determined in a comparative way by the spread plate method.100 μ L of culture suspension was collected from well and spread over the LB agar plates with appropriate dilutions and then incubated at 37°C for another 24 h under static condition. The killing efficiency was determined by counting bacterial colonies compared to control.

2.5. Molecular docking

DNA gyrase and DNA polymerase III (Pol III) are two essential proteins required for bacterial DNA replication with high efficiency and accuracy which leads to bacterial cell viability [96,97]. DNA gyrase catalyzes the ATP-dependent negative supercoils into DNA and Pol III carried out highly processive DNA replication during cell division in tight coordination between synthetic strands. These two proteins of bacteria serve as the potential targets in the development of new antibacterial compounds. Molecular docking was performed using *Escherichia coli* DNA gyrase (GyrB) and DNA Pol III protein. The crystallographic structure of both proteins: GyrB (PDB ID: 5MMN, resolution=1.9 Å) and Pol III (PDB ID: 2HNH, resolution=2.3Å) were downloaded from RCSB Protein Data Bank (PDB) [https://www.rcsb.org/pdb].

2.6. Synthesis of N, N-bis(3-methoxysalicylidene)-2,2-dimethylpropane-1,3 diamine

Schiff base has been synthesized in our laboratory following the literature method (Scheme 1) [98]. It was obtained by the reflux condensation of 2, 2-dimethyl-1, 3-propanediamine (0.0511 g, 0.5 mmol) with 3-methoxy-2-hydroxybenzaldehyde (0.152 g, 1 mmol) in (50 mL) methanol at 70 °C for 3 h. Subsequently solvent was removed under vacuum to give a yellow powder product. N, N-bis(3-methoxysalicylidene)-2,2-dimethylpropane-1,3 diamine: Yield: 0.158 g (85.4 %), Anal. Calc. for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56 Found: C, 68.06; H,

7.05; N, 7.53 %. IR (KBr cm⁻¹) selected bands: v(C=N), 1652 vs, v(C-O_{phenolic}) 1252 s, v(O-H) 3378 s, ¹H NMR (DMSO-d6, 300 MHz): δ (ppm): 3.76 (s, 3H¹), 6.79-7.01 (m, 1H², 1H³, 1H⁴), 8.50 (m, 1H⁵), 13.86 (m,1H⁶), 3.45-3.46 (s, 2H⁷), 0.96 (s, 6H⁸), (Scheme1, Fig. S3A), ¹³C NMR (DMSO-d6, 75.45 MHz): δ (ppm):15.2 (¹¹CH₃), 64.2-67.0 (O-¹CH₃),116.3-147.6 (Arom-³C-⁵C),152.2 (⁷C-OH), 167.3 (⁸CH=N), 24.0 (¹⁰C-(CH₃)₂, 36.1 ((CH₃)₂-C-(⁹CH₂)₂), (Fig. S3B), UV-Vis (λ_{max} /nm): 382 nm.



Scheme 1 Synthesis of compartmental Schiff base ligand (H₂L^{OMe-pn})

2.7. Synthesis of complex as single crystal

To the methanolic solution (25 mL) of zinc acetate dihydrate (0.2195 g, 1 mmol), (10 mL) ligand solution was added drop by drop and the resulting solution was stirred for 1 h. Then (10 mL) methanolic solution of Ca (SCN)₂.4H₂O (0.228 g, 1 mmol) was added to it. The overall reaction mixture was refluxed for 30 min at 85 0 C followed by adding few drops of DMF. Stirring was continued for about 1.5 h. Colourless filtrate was kept for crystallization by slow evaporation at room temperature. Single crystal, suitable for X-ray diffraction was obtained after 25 days on slow evaporation of the solution in open atmospheric condition. Colourless block shaped crystals were isolated by filtration and air dried. Yield: 0.53 g, (51.8 %), Anal. Calc. for C₄₄H₄₈ CaN₆O₈S₂Zn₂: C, 51.61; H, 4.73; N, 8.21. Found: C, 51.59; H,

4.70; N, 8.25 %. IR (KBr cm⁻¹) selected bands: v(C=N), 1624 vs, v(C=N), 2215 s, v(SCN) 2090 vs, FT-Raman (cm⁻¹) selected bands: v(C=N), 1632 vs, v(C=N), 2191 s, v(SCN) 2106 vs, ¹H NMR (DMSO-d6, 300 MHz): δ (ppm): 3.76 (s, 3H¹), 6.78-7.10 (m, 1H², 1H³, 1H⁴), 8.42 (m, 1H⁵), 3.35 (s, 2H⁶), 0.96 (s, 6H⁷), (Fig. S3C), ¹³C NMR (DMSO-d6, 75.4 MHz): δ (ppm):14.9 (¹¹CH₃), 64.5-65.7 (O⁻¹CH₃), 115.5-151.7 (Arom-³C-⁵C), 164.4-166.6 (⁸CH=N), 20.5 (¹⁰C-(CH₃)₂, (Fig. S3D), UV-Vis λ_{max} (DMSO): 370 nm.

3. Results and discussion

3.1. Synthetic aspect

Schiff base was synthesized by the condensation of 2, 2-dimethyl-1, 3-propanediamine with *ortho* vanillin (3-methoxy-2-hydroxybenzaldehyde) in MeOH at (1:2 M) ratio (Scheme1) [98]. The complex was derived in moderate yield by taking the following in situ procedure where (1:1:1 M) ratio of Zn(II) acetate dihydrate, hexadentate N₂O₄ proligand and Ca(SCN)₂.4H₂O in minimum volume methanolic solution under stirred and reflux condition followed by a few drops of DMF (Scheme 2). After few days moderately air stable block shaped crystals appeared at the junction of the solutions which are insoluble in water. Interestingly, Zn(II) is placed in inner N₂O₂ compartment and Ca(II) is placed in an outer O_2O_2 compartment of the respective N_2O_4 proligand. Since Ca(II) centres were well surrounded by the alkoxy group, therefore pseudo-halides (thiocyanate) were unable to coordinate Ca(II) centre. Further, such stereochemical difference is probably due to the larger size Ca(II) metal ion (ionic radius 126 pm) compared to that of small size Zn(II) ion (ionic radius 74 pm). Hence it is difficult to accommodate large size Ca(II) in the inner N₂O₂ compartment compared to that of external cavities O_2O_2 [87]. This stereochemical environment is completely comparative with already detailed salen-type bi-compartmental M¹(II)/M²(II)-Schiff base complexes [52,98,99]. Moreover, Salicylaldehyde derivatives (ortho vanillin) are useful precursor for novel syntheses of Schiff base since additional

alkoxy group attached to salicylaldehyde not only enhanced the ligand denticity but accelerated the discrete or polymeric complex formations [71]. Binding versality of N_2O_4 proligand with metal ions is another responsible factor for its selection of the current research work (Scheme S1). Scheme 3 totally discloses N_2O_4 proligand basic imitates since it comprises two imines, two phenols and two methoxy groups. After deprotonation, N_2O_2 imine chelating location is produced which is facilitated with M^{2+} metal ions (Scheme 3) [100]. In most of the hetero-metallic complexes entangling capability of metal ions (Scheme 3) by inward N_2O_2 and external O_2O_2 ' compartments was investigated strikingly [52,83,99] however, till date hetero-nuclear Zn(II)/Ca(II) complex with particular hexadentate N_2O_4 proligand is cruelly lacking in the literature [18,101].



Scheme 2 Synthetic route for hetero-bimetallic complex. A=Zn(OAc)₂.2H₂O,

B=Ca(SCN)₂.4H₂O, C=Few drops of DMF



Scheme 3 Existing compartmental ligand showing N₂O₂ vs O₂O₂ pocket

4 | X-ray crystallography

4.1. Crystal structure of $[Zn_2(L^{OMe-pn})_2(\eta^1-NCS)_2Ca]$ (1)

The complex is structurally characterized by single crystal X-ray diffraction, and it reveals that it crystallizes in monoclinic space group $P2_1/c$ (Z=8). The complete crystallographic parameters are shown in Table 1 and selected some important bond distances (Å) and angles (°) are shown in Table S1.The ORTEP view of asymmetric unit (Fig.1) contains two molecular units which cooperate by a few C-H···· π type non-covalent associations portrayed in Fig.3 reflecting Ca-O bond distances (Å). A close investigation into the complex crystal structure reveals that the asymmetric unit contains two Schiff base ligands (L^{OMe-pn}), (where H₂L^{OMe-pn} is the diprotic proligand), two Zn atom and one Ca atom (Fig.2). Further from ligand structural point of view, the hexadentate N₂O₄ proligand has two pockets, one is occupied by Zn(II) ions and other is occupied by Ca(II) ion. In each molecular unit the Zn(II) centre is fitted into the N₂O₂ compartment with the η^1 fashion of NCS⁻ co-ligand with distorted square pyramidal geometry. This structural motif is identical with previously reported heterometallic complexes [52,83,99,102].



Fig.1. ORTEP view of the asymmetric unit (Hydrogen atoms are omitted for clarity)



Fig.2. Two molecular units in the asymmetric unit (Hydrogen atoms are omitted for clarity)



Fig.3. C-H···· π type non-covalent interactions

In complex **1**, two salen ligands are almost in perpendicularly (83.15° and 80.92°) oriented by Ca(II) metal ion. The Ca(II) metal ion in each unit is coordinated to eight oxygen atoms, half is coming from phenolic group and half is coming from methoxy group. Overall, this stereochemical environment is similar with previously reported Ca(II)-Salen complexes [99,101]. In the asymmetric unit (Fig.2), Ca1 is coordinated to O1 to O8 oxygen atoms and Ca2 is coordinated to O9 to O16 oxygen atoms. The equatorial plane of all the Zn(II) ions are occupied by N₂O₂ compartment of salen ligand and apical position is occupied by the N atom of thiocyanate group. The Zn(II) centres (Zn1-Zn4) are displaced towards axial N3/N6/N12/N9 atom by 0.523 Å, 0.512 Å, 0.520 Å, and 0.512 Å, respectively from their respective mean equatorial planes. The synthesized complex exhibit awesome C-H… π type non-covalent interactions (Table2) which is rehashed all through the 3-D sheet of Packing diagram (Fig.S5A).

Table 2 C-H···· π type non-covalent interactions

Components	Distance (Å)	Angle (°)
С12-Н12А	3.182 (3)	160.65(5)
С55-Н55π	3.83 (3)	154.61(5)
C13-H13AN8	3.34 (5)	128.22(5)
C53-H53AN4	3.49 (5)	124.95(5)

Further, the structural environment of two zinc metal centres were calculated from Addison parameter Tau (r), (r = $|\beta - \alpha|/60^\circ$ where β , α are the two largest angles around zinc metal atom; r = 0 for a perfect square pyramidal and 1 for a perfect trigonal bipyramidal geometry [103]. The calculated Addison tau (τ) parameters are 0.098, 0.145, 0.063, and 0.21 (ideal value of tau for square pyramidal geometry is 0) respectively, for four Zn(II) centres. The large open O₂O₂' compartment is occupied by octacoordinated Ca(II) metal ion, resulting a tri-nuclear hetero-bimetallic system. The average distances between two heteroatoms (Zn and Ca) is 3.530 Å {Zn1-Ca1 = 3.5195(12), Ca1-Zn2 = 3.5318(13), Zn3-Ca2 = 3.5237(13), Zn4-Ca2 = 3.5453(13) and the average angle between them is 106.33 ° {Zn1-O1-Ca1 = 105.79(16) °, Ca1-O3-Zn1 = 105.20(15)°, Ca1-O5-Zn2 = 106.96(18)°, Zn2-O7-Ca1 = $106.83(18)^{\circ}$, Zn3-O9-Ca2 = $105.66(16)^{\circ}$, Zn3-O11-Ca2 = $106.21(16)^{\circ}$, Ca2-O13-Zn4 = $107.38(17)^\circ$, Ca2-O15-Zn4 = 106.62(17)°. The bond lengths of Zn-N_{thioevanato} are in the range of ~1.981–2.091 Å which are comparable with literature reported Zn(II) complexes (Table S3). In the meantime, to underline as-blended complex structure, we have demonstrated an auxiliary correlation with literature reported hetero-nuclear complexes (Table S5A-S5B). To the best of our knowledge this is the first ever example of heterobimetallic system where two terminal Zn(II) centres are appropriately fit into the N_2O_2 compartment followed by large open O_2O_2 ' compartment possessed by Ca(II) ion.

4.2. SEM-EDAX

To find out the chemical composition of complex **1**, SEM-EDAX analysis was performed. The chemical composition of **1** was confirmed from EDAX profile analysis. The weight percentage (%) contribution of the elements is submitted in Table S4 and their EDAX profile in Fig.S6. The calculated and EDAX values of essential elements present in complex are nearly good agreement. EDAX profile contained only predictable elements and there is no impurity of other elements. Therefore, the empirical formula of **1** is formulated as $C_{44}H_{48}CaN_6O_8S_2Zn_2$. Interestingly, the EDAX profile of complex reflects the highest peak of C and thereafter O, N, Zn which further agreed the empirical formula of **1**. Moreover, the important structural morphological features are supported by SEM investigation. SEM images characterized the size and morphological structure. Herein, micrograph of SEM (Fig.S7A) clearly explores that the morphology of **1** is plate shape shown up to 50 µm.

4.3. Powder X-ray diffraction

Powder X-ray diffraction patterns for 1 were recorded at room temperature. The X-ray powder diffraction patterns for complex were recorded experimentally by scanning the synthesized complex in the range $(2\theta=4^{0}-50^{0})$ using 1-D Lynxeye detector at ambient conditions. Fig.S7B show well defined sharp PXRD peaks due to their crystalline nature. The experimental PXRD patterns (Fig.S7B) of the bulk materials of heteronuclear complex are similar with the patterns simulated from single crystal X-ray diffraction data (CIF) obtained from CCDC Mercury software consisting that single crystals and bulk material are the same. The results of PXRD analysis can provide the confirmation of the phase purity of each bulk samples.

5. DFT analyses

5.1. Hirshfeld surface

Apart from SCXRD analysis, short intermolecular contacts in the crystal structure of the complex can be quantified by Hirshfeld surface and 2D fingerprint plot. Hirshfeld surface (HS) is one of the emerging attempts to define the space occupied by a molecule in a crystal after proper partitioning the crystal electron density into molecular fragments [104]. HS and 2-D fingerprint plots were generated to visualize, explore and quantify the short intermolecular interactions in the supramolecular packing where Crystal Explorer program [105] has been commonly used. Herein, such analyses revealed the presence of important short intermolecular contacts like C···H/S···H/ N···H/O···H/H···H/C···C and S···S in the crystal structure. The HS mapped with the d_{norm} property has been shown in the Fig.4 and the 2-D fingerprint plots with characteristics features of their short interactions are represented in Fig.4(a-c). The dominant interactions according to HS mapped with d_{norm} are the red spot. In 1, relative contributions to the HS area due to close intermolecular contacts are as follows: C...H, 45.8%; S...H, 33.8%; N...H, 9.2%; O...H, 3.2%; H...H, 51.0%; C...C, 0.6%; and S...S 0.8 % (Table 3). HS analysis divulges that the assembly dominated by H…H and C…H supramolecular contacts along with minor contributions C···C/S···S. In terms of 2-D fingerprint plots (Fig.4), the intermolecular interactions appear as distinct spikes. Details breakdown of HS and 2-D fingerprint plots of different contributions are submitted in Fig.S8.



Fig.4. Hirshfeld surface d_{norm} property: red spot represents closet contacts and blue spot most distant contacts. Graphical view of Hirshfeld surface and 2-D fingerprint plots with

chacteristics features of C···H 4(a) S···H 4(b) N···H 4(c) contacts, di and de are the distances

from the surface to the nearest atoms interior and exterior to the surface

SL. No.	Type of interactions	Major contribution (%)
1.	$C \cdots C$ (i.e. $\pi \cdots \pi$)	0.6
2.	$C \cdots H$ (i.e. $C - H \cdots \pi$)	45.8
3.	$S \cdots H$ (i.e. $C - S \cdots H$)	33.8
4.	N····H	9.2
5.	H···· O	3.2
6.	H···H	51.0
7.	S····S	0.8

 Table 3 Different type of interactions on HS in complex 1

5.2. Total energy Frameworks (TEF)

The Crystal Explorer program [105] has been used for energy framework calculation in favour of synthesized complex. The molecular packing in the unit cell was explored by means of energy frameworks analysis. Accordingly, the interaction energies between different molecular pairs are represented via cylindrical tubes connecting the centres of mass of the interacting molecules. The radius of the cylindrical tube is directly proportional to the interaction energies. Further insight can be gained when the topology, which is represented by cylindrical tubes, is disintegrated into electrostatic and dispersive components [106,107]. In complex 1, total-energy-framework diagram exhibits a relatively isotropic topology of interactions where the dispersion component (-74.5 KJ/mol) is dominating over others. The occurrence of dimer in the asymmetric unit of complex is certainly stabilizing, with a total energy of -106.5 KJ/mol. Fig.5(a-c) reflects electrostatic, dispersive, and total energy contribution. The calculated energy frameworks output is submitted in Table S6.



Fig.5. (a) Electrostatic, (b) dispersive and (c) total energy contribution



Fig.6. (a) Electrostatic, (b) dispersive and (c) total energy contribution in the asymmetric unit

5.3. MEP

Molecular electrostatic potential (MEP) were calculated to comprehend the relationship between the molecular structure and reactivity towards nucleophilic and electrophilic regions. Because of the electron density distribution, MEP is described as the potential experienced by a unit positive charge near the molecule. MEP indicates the relative polarity of the molecule as positive potential can predict electrophilic attack sites while the adverse potential indicates sites for nucleophilic attack. The expression for the MEP at any point r in the space near the molecule is given by equation (4)

$$V(r) = \sum \frac{z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|}$$

(4)

Where, Z_A is the charge on the nucleus A studied at R_A and $\rho(r')$ the electron density. V(r) defines the net electrostatic effect of the total charge distribution (electrons + nuclei) of the molecule at point r. MEP mapping has recently played a notable part in the geometric structure, charge density analysis and polarity of various molecular systems [102,108,109]. MEP was generated from the DFT optimized structure of the synthesized complex to visualize electrophilic and nucleophilic regions (Fig.S8A). Moreover, MEP map distribution purpose Multiwfn program [110] and the FChk type file was used as the input program using at B3LYP/6-31G (d, p) level of theory. The red colour on the molecular surface in the Fig.8A shows the negative MEP (areas prone to nucleophilic attack) while the blue colour on surface shows positive MEP (electrophilic attack). The potential on MEP surface of the complex is in the following order of yellow < orange < red < green < blue. The green colour on the surface indicates the region with zero potential. Further it is evident that the regions around the terminal Sulphur atoms of the two thiocyanate co-ligands have the highest negative electrostatic potential with a value of -48.9 kcal/mol and the highest positive charge is found near the azomethine hydrogen atoms with a value of +46.1 kcal/mol (Fig.S8B). This is common nature found widely among the salen-type complexes [111,112]. The region around the Zn metal centre has a positive charge of +21.6 kcal/mol while the benzenoid rings of the complex have a charge of -26.4 kcal/mol. The area around calcium metal ion where it is bonded by eight oxygen atoms appears to have a negative charge of about -36.5 kcal/mol.

5.4. Global reactivity

Global reactivity descriptors can be taken as a tool for reactivity and regioselectivity of the synthesized compound towards various reactions [113] which are also carefully calculated in

Table S6A. On performing Mulliken charge analysis (Fig.S8B), it reveals that the highest positive charges are concentrated on the metal centres. Out of the three metal centres, only Ca centre has a charge of +1.17 and the two Zn centres have a charge of +0.96 each. The highest negative charges are concentrated on the donor hetero atoms (S, N, O) and among them phenolic oxygens of the salen-type ligand exhibited the highest charge (-0.77) followed by methoxy oxygen atoms in these ligands (-0.58). The next highest charge is observed in nitrogen atoms of the thiocyanate co-ligand (-0.57) and by the azomethine nitrogen atoms (-0.46). The least negative charge is observed in sulphur atoms (-0.29) of the coordinated thiocyanate moiety.

5.5. TD-DFT

TD-DFT computations were executed in DMSO solvent to quantify the contributions of various frontier molecular orbitals (FMO) towards absorption spectra (Table S6B). It is evident that major molecular orbital contributor in charge transfer (CT) region in complex **1** is HOMO-LUMO (Table S6B). The computed TD-DFT study of complex **1** exhibits the electronic transitions which are mainly due to the intra-molecular charge transfer. The HOMO of the complex is mainly composed of π -orbitals whereas LUMO consists of π^* -orbitals. The analysis of calculated spectrum disclosed one strong electronic transition at 365 nm (experimental 370 nm) with oscillator strength 0.33 (Fig.S9 and Table S6B). The electronic transition is primarily due to the transition of an electron from HOMO to LUMO (48%) and HOMO to LUMO-1 (22%).

5.6. Energy and HOMO-LUMO analysis

Synthesized complex was optimized in DMSO solvent using a PCM model including solvent effect at M06/6-31G* level of theory. Fig.S10 shows the optimized geometry of complex **1**. The mapping of the frontier molecular orbitals (FMOs) has provided an interesting outcome

for complex. HOMO (highest occupied molecular orbital) value determines a molecule's capacity to donate electron while LUMO (lowest unoccupied molecular orbital) value determines the electron-accepting nature. HOMO-LUMO density plot (Fig.7) was used for probing of FMOs of the complex as it is well known that the non-linear optical (NLO) characteristics of π -conjugated complexes are derived from the delocalization of the π electron cloud [114]. A close inspection of the HOMO-LUMO energy plot divulges that HOMO of 1 is primarily contributed from the methoxy group (donor) and oxygen atoms which is coordinated to the Ca-atom at the centre of the molecule. In LUMO, the electron density is mainly focused on the moieties which are attached to the methoxy group and other moieties which are bridged with nitrogen atoms connected to the zinc-atoms. The [SCN] spacer makes the bridging is strong and stable since it is not contributing much in HOMO or LUMO and it affects the stability of the complex. The electronic energy of HOMO-LUMO is tabulated in Table S6C. The energy of HOMO is -5.73 eV whereas of LUMO is -1.46 eV. The energy gap ΔE of HOMO-LUMO ($\Delta E = E_{LUMO} - E_{HOMO}$) is 4.27 eV (marked by blue line, Fig.7) which is slightly high making the complex stable and can be correlated with the band gap of the complex. The distinction between the conductive band and the valence band is usually referred as the band gap. In order to check the semiconducting properties of complex, theoretical UV-Vis absorption spectra were also calculated and shown in Fig. S9 (wavelength range of 200-600 nm). Here the theoretical band gap is in the range of 3-6 eV which is defined for the wide-band gap semiconductors [115,116]. Therefore, complex possesses semiconducting property. Because its bandgap is about 4.27 eV (wide-bandgap semiconductor), it functions at much greater voltages, frequencies and temperatures than usual semiconductor-based products. Based on these theoretical bandgap, compound 1 can be suitable for next-generation semiconductor devices.



Fig.7. Frontier molecular orbitals of 1 (ΔE : Energy gap between HOMO and LUMO)

5.7. NLO activity

The energy gap ΔE (4.27 eV) is linked to the transfer of electron density from the HOMO to the LUMO and its value is important for the determination of the NLO property of the molecular system. If a molecule possesses a smaller energy gap generally shows high NLO activity [117]. Herein, theoretical calculations support the mentioned findings. In complex **1**, various parameters such as electric dipole moment (μ), polarizability (α) and first hyperpolarizability (β^{hyp}) were computed at the M06/6-31G* level of theory (Table4), Since the first hyperpolarizability (β^{hyp}) value is equal to 59.62 × 10⁻³¹ esu, synthesized compound exhibit good NLO activity which may be due to the increased distribution of π -electronic charge at the ground state by the donor and acceptor moieties under the impact of an electrical field. In addition, β^{hyp} is often associated with the charge transfer bands resulting from the electron cloud movement through the π -electronic framework from donor to the acceptor level, and such electronic clouds interact with external fields, resulting in an increase in β^{hyp} . The α and β^{hyp} values are directly indicated that synthesized complex exhibits good NLO activity.

Table 4 DFT computed dipole moment (μ), average polarizability (α) and first hyperpolarizability (β^{hyp})

Complex	μ (Debye)	α (10 ⁻²² esu)	β^{hyp} (10 ⁻³¹ esu)
$[Zn_2(L^{OMe-pn})_2(\eta^1-NCS)_2Ca] (1)$	14.44	0.58	59.62

6. Spectroscopic analyses

6.1. FT-IR and Raman characterizations

Ligand and complex were characterized by the IR spectroscopic methods. The characteristic imines (C=N) stretching vibration of synthesized Schiff base was found to be 1652 cm⁻¹ [118] (Fig.S1). FT-IR and Raman (C=N) stretching vibration bands are shifted to 1624 cm⁻¹ (for IR) (Fig.S2) and 1632 cm⁻¹ (for Raman) respectively (Fig.S3), These spectral data confirms the coordination mode of the imine nitrogen atom to the Zn(II) metal centre [119]. Complex displayed strong bands at 2090 cm⁻¹ (for FT-IR) and 2106 cm⁻¹ (for FT-Raman) [120,121]. These spectral values are directly attributable to v(SCN) binding mode. Aliphatic C-H stretching resonances are observed at 2932-2964 cm⁻¹ (for FT-IR) and 2916 cm⁻¹ (for FT-Raman) respectively. Ar-O stretching frequency near 1219 cm⁻¹ is identical with previously reported salen-type ligands [122]. Herein, the bridging mode of [SCN⁻] spacers in the light of IR/Raman spectra were thoroughly compared with previously reported Zn(II)-Schiff base complexes (Table S2A-Table S2B).

6.2. UV-Vis spectra

The UV-Vis absorption spectra of the Schiff base and its complex were recorded in DMSO solvent. Free ligand exhibit band at 382 nm (Fig. S4) which are assigned due to $\pi \rightarrow \pi^*$ and

 $n \rightarrow \pi^*$ type transitions whereas complex displayed sharp single ligand-based UV domain at 370 nm attributed to L \rightarrow M charge transfer transition ($\pi \rightarrow \pi^*/n \rightarrow \pi^*$) (Fig.S4) [119,123]. The spectral domain supports the coordination mode of the ligand with Zn(II) metal ions which are blue-shifted 12 nm. The blue-shift may be due to the structural environment of ligand and the perturbation of the intraligand $\pi \rightarrow \pi^*$ transition by the Zn(II) ions which are nearly comparable with previously reported Zn(II) salen-type complexes [123b]. Here no metal centric d-d broad absorption band was assigned due to d¹⁰ electronic configuration and diamagnetic nature of Zn(II) metal ion.

6.3. ¹H and ¹³C NMR spectra

¹H and ¹³C NMR spectra has been used to extract the formation of Schiff base ligand and its coordination mode with Zn(II) ion in as-synthesized complex (Scheme 1). ¹H and ¹³C NMR spectral data of ligand and the complex was provided in the experimental section. Free Schiff base no broad peak was identified in the region δ 5.0-8.0 ppm indicating the absence of the free -NH₂ group. Moreover, the identified broad peak at δ 13.86 ppm corresponds to the phenolic (OH^{6}) protons. The protons (H^{5}) attached to the imino carbon are strongly downfield shifted (δ 8.5 ppm) [124] due to the influence of the combined effect of phenolic -OH and imino N groups in its close vicinity. The peaks near the range δ 6.79-7.01 ppm corresponds to the aromatic protons (H^2-H^4) . The three methyl protons OCH₃ (H^1) attached to the aromatic oxygen appear at δ 3.76 ppm. Apart from, (C-(CH₃)₂ group protons (H⁸) appear at δ 0.96 ppm. Since methylene protons (H') being very close to the imino nitrogen, are deshielded and appear at δ 3.46 ppm. In case of complex, the coordination mode of azomethine (HC=N) nitrogen was assigned by the downfield shifting of the azomethine proton signal from 8.50 ppm in free Schiff base to 8.42 ppm. Moreover, the OH proton (OH⁶) signal at the Schiff base disappeared in the ¹H NMR spectra of the synthesized hetero-nuclear complex, indicating deprotonation and coordination of the oxygen with Zn(II) ion [125]. The ¹³C NMR spectra of Schiff base ligand showed characteristic azomethine (${}^{8}CH=N$) carbons at 167.3 ppm. The other ${}^{13}C$ NMR peaks observed at 15.2 (${}^{11}CH_3$), 64.2-67.0 (O- ${}^{1}CH_3$), 116.3-147.6 (Arom- ${}^{3}C-{}^{5}C$), 152.2 (${}^{7}C-OH$), 24.0 (${}^{10}C-(CH_3)_2$ and 36.1((CH_3)₂-C-(${}^{9}CH_2$)₂) ppm respectively (Fig.S3B). Downfield shifting of the azomethine carbons in the free ligand 167.3 ppm to 164.4-166.6 ppm in its Zn(II) complex was due to shifting of electron density towards the Zn(II) ion. This downfield shifting also confirmed the coordination of the azomethine to the zinc metal atom (Fig.S3D) [125,126].

7. Steady-state photoluminescence

Fluorescence spectral properties of Schiff base ligand and complex are determined in DMSO solvent at room temperature. According to Fig.8 the free ligand demonstrated a fluorescence peak at ca 489 nm upon excitation at ca 370 nm which could be attributed to intra-ligand $(\pi \rightarrow \pi^*)$ type transition whereas for complex 1 photo excitation at similar wavelength shows red shifted fluorescence maxima with the major emission peak at ca 505 nm. The enhancement of fluorescence emission intensity of 1 over free ligand probably may be due to N/O-donor centres coordination with the Zn(II) metal ion, thereby increasing the conformational rigidity via chelation effect and subsequently loss of energy by radiation less thermal vibration. Meanwhile, the active fluorescence spectral change compared to free ligand may be due to d¹⁰ electronic configuration of Zn(II) metal ion which is difficult to oxidize or to reduce. This fluorescence behaviour may be attributed to the intra-ligand $(\pi \rightarrow \pi^*)$ type transition or L \rightarrow M charge transfer referred as CHEF (Chelation enhanced fluorescence) [127-131]. The enhancement of emission intensity of complex (about 16 nm) over ligand is supported by quantum yield ($\Phi_{\rm F}$) values with reference to quinine sulphate (Table 5). Generally, fluorescence emission of Schiff base ligands containing an aromatic ring enhance or quench in contact with metal ions. Herein a close inspection of quantum yield value confirmed that variations are negligible. This is due to the excitation wavelength of

ligand and complex are identical, which further divulges that synthesized compounds are fluorescence in nature where strong electronic coupling between the neighbouring ligand through Zn(II) ions takes place, thereby facilitates fast photoinduced electron transfer (PET) process from nitrogen lone pair to the conjugated phenolic moiety. After coordination of ligand with the Zn(II) metal ion increase the rigidity of the ligand, prevents the PET process, thereby considerable enhance of quantum yield (ϕ) value [132,133]. The synthesized complex is hetero-bimetallic, hence we have considered fluorescence response is attributed only for Zn(II) ion but not Ca(II) metal ion. To emphasize the underlying area, we have cited literature-based fluorescence response for Zn(II) and Ca(II) related metal complex, e.g. Ca(II)NDC-MOF exhibits blue shift $L \rightarrow M CT$ fluorescence response with respect to free organic linker H₂NDC (1,4-naphthalenedicarboxylic acid) but enhanced red shifted after incorporation of d¹⁰ group of Zn(II)/Cd(II) metal ions. The blue shift may be due to the incorporation of Ca(II) metal ion within the cavity of organic linker H₂NDC ((1,4naphthalenedicarboxylic acid) [111]. Moreover, P^H dependence fluorescence activity of Cachelates with HQS (8-Hydroxyquinolin-5-Sulfonic acid) further confirmed blue shift fluorescence over Zn(II)/Cd(II)/Hg(II) metal ions [134]. Conclusively, calcium metal ion has no impact for red shifted fluorescence. To the best of our knowledge this is the first heterobimetallic system fluorescence activity which divulges the opportunity for next generation photochemical applications.



Fig.8. Ligand-centered fluorescence emission spectra

 Table 5
 Summary of steady-state photoluminescence for ligand and complex

Ligand λ _{ex} (DMSO)	(nm)	λ_{em} (nm)	Quantum Yield (ϕ)	
Schiff base	370	489	0.0345	
Complex (DMSO)		$\lambda_{ex}(nm)$	$\lambda_{em}(nm)$ Quantum Yield (ϕ)	
$[Zn_2(L^{OMe-pn})_2(\eta^1-NCS)_2Ca]$] (1)	370	505	0.0487

8. Antibacterial activity

At first, we have systematically analysed the concentration dependent antibacterial activity against various model test organisms such as *E. coli*, *P. aeruginosa*, *S. aureus* and *B. subtilis*. Concentration dependent antibacterial assay (Fig.8) directly confirms that complex **1** has excellent antibacterial efficiency against wide range of gram-negative and gram-positive bacterial strains. Complex **1** inhibited more than 50% cellular growth at concentration 10 μ M

for *E. coli* (Fig.9a) as well as for *S. aureus* (Fig.9c) and at concentration 5 μ M for *P. aeruginosa* (Fig.9b) as well as for *B. subtilis* (Fig. 9d). The growth inhibition efficiency was increased on increasing the concentration of complex **1**. Analysis revealed that the antibacterial efficiency of complex **1** was significantly higher than the efficiency of Schiff base ligand (L1). This bacterial feature is common for other d¹⁰ group metal Schiff base complexes [135]. The enhanced antimicrobial activity of complex **1** over ligand is due to 'Overton concept' of cell permeability and the 'Tweedy chelation theory' [136,137]. It is worth to mention that solvents (CH₃OH & DMSO) did not show any significant antibacterial activity (Fig.10) against the tested microorganisms. Thus, it can be inferred that no solvent effect was came in this scenario and the antibacterial effect was originated exclusively from the complex **1** [137].



Fig.9. Concentration dependent growth inhibition efficiency of complex and ligand against (a) *Escherichia coli* (b) *Pseudomonas aeruginosa*, (c) *Staphylococcus aureus* and (d) *Bacillus subtilis*



Fig.10. Solvent (Methanol and Dimethyl sulfoxide) effect on bacterial (Escherichia coli,

Pseudomonas aeruginosa, Staphylococcus aureus and *Bacillus subtilis*) growth in LB We have also investigated the killing efficiency of complex **1** compared with that of ligand (L1) through the formation of bacterial colonies on agar plate. The detail results have been shown in Fig.11. The results revealed that complex **1** efficiently killed both gram-positive and gram-negative bacterial cells with the inhibition of their growth. In case of complex **1**, treated bacterial suspension, lesser number of bacterial growths were found in each test organism on agar plate compared to control and ligand (L1) treated bacterial suspension. Thus, it can also be said that the killing efficiency of complex **1** is much higher than ligand (L1). This effect is similar to the reported Zn(II)-Schiff base complex **[138]**. Therefore, complex **1** behave as both bacteriostatic and bactericidal effects **[138]**.



Fig.11. Bacteria killing efficiency of C1 and L1 against (a) *Escherichia coli* (b) *Pseudomonas aeruginosa*, (c) *Stophylococcus aureus* and (d) *Bacillus subtilis*

9. Molecular docking

The synthesized complex **1** was docked favorably (de-solvation energy -239.49 kcal mol⁻¹ and 260.27 kcal mol⁻¹, score = 4750 and 5252, respectively) inside the catalytic region of GyrB and Pol III (Table S7 and Fig.12). Crystal structure of the complex **1** bound to *E. coli*. GyrB forms several interactions contributing to its affinity to hydrogen bonds with Asn46, Asp49, Glu50, and Asp73, alkyl hydrophobic bonds with Arg76 and Pro79, π stacking interactions between Asp49, Ala53 and Ile94 (TableS8). Simulated docking showed that the tested complex might be anchored into the palm region of Pol III with favorable de-solvation energy through residues like Gln429, Ile430, Thr432, Lys510, His511, and Asp531 (for H-

bonding). Ala508, Ala512, Tyr529, and Val538 were the other amino acids found in this complex forming $\pi - \pi$ and π – alkyl interactions (Fig.12).



Fig.12. Molecular docking analysis of two proteins GyrB (A1 & A2) and PoIII (B1 & B2) with complex 1 (A2 and B2 show the illustration of ligand-amino acid interactions within the docked complex)

Inhibition of DNA unwinding and DNA replication exhibited a potent antibacterial activity against a broad range of bacteria. In this study, complex **1** form the H-bond with Asp73 which is the conserved amino acid found in the ATP binding site of *E. coli* DNA gyrase [96]. This ATPase domain also consists of common residues like Glu50 and Arg76 which were also noticed in this protein-ligand complex. So, it can be predicted that synthesized complex

has the potentiality to inhibit the ATPase activity of DNA gyrase, thus blocking the energy source required for DNA replication. The main active site of the DNA Pol III is located within the palm domain which is formed by the residues 271-432 and 511-560 of that protein [97]. Complex 1 can interact with the amino acids Gln429, Ile430, Thr432, His511, Ala512, Tyr529, Asp531, His536, and Val538 which are the part of this catalytic region of Pol III. Though we didn't find any interaction with the catalytic Asp401, Asp405 and Asp555 in our docking experiments but our study could speculate that the tested complex can bind with the outer shell of that catalytic cavity and may lead to the unviability of the palm domain for DNA during replication.

10. Concluding remarks

This paper describes synthesis, structural characterization, spectroscopic properties, DFT/TD-DFT study and biological activity of a new hetero-bimetallic Zn(II)/Ca(II) complex, $[Zn_2(L^{OMe-pn})_2(\eta^1-NCS)_2Ca]$ (1). Single crystal X-ray diffraction revealed that compound 1 is hetero-nuclear structural motif in which large size Ca(II) ion is accommodated at the outer O_2O_2 compartment, whereas Zn(II) metal ions at the inner N_2O_2 cavities. As-synthesized complex display fascinating C-H···· π type non-covalent interactions in the crystal packing. Some significant DFT based investigations, as Hirshfeld surface, FMO, MEP, Global reactivity and NLO have been carried out. Photophysical properties have been investigated to find out the origin of emission spectra. In *vitro* antibacterial activity of the ligand and the complex was performed against gram-negative and gram-positive bacterial strains. While comparing the results, it is inferred that complex exhibits better antimicrobial activity than ligand against all the tested microorganisms. As a comparative mode of approach, bacterial killing efficiency and solvent effect have been explored for ligand and complex. The experimental findings were corroborated by the Molecular docking study with DNA gyrase and DNA polymerase III proteins. We envision the current examination will irrefutably open a novel synthetic route for antimycobacterial agents in the crystal engineering domain.

Conflicts of interest

All authors declare no competing interest regarding the article publication.

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AUTHOR CONTRIBUTION

1. **Dhrubajyoti Majumdar**—Principal Investigator, Conceptualization, Methodology, contributed synthesis, Characterizations, data collection, Software, visualization, Writing-review and Editing, Writing-Original draft preparation and Editing, Formal analysis and performed all necessary works.

2. Dhiraj Das-Collected the X-ray data for synthesized complex

3. Sudip Nag and Maitree Bhattacharyya -data collection for antibacterial analysis

4. Dheeraj K. Singh-performed theoretical DFT study

5. Debaprasad Parai- Software, visualization

6. Kalipada Bankura- assistant to the Principal Investigator

5. Dipankar Mishra- Ph.D. supervisor. He is also the corresponding author.

CREDIT AUTHOR STATEMENT

1. Dhrubajyoti Majumdar: Data curation, Conceptualization, Methodology, Investigation, Software, visualization, Writing-review and Editing, Writing-Original draft preparation and Editing, Formal analysis

2. Dhiraj Das: Software, visualization

3. Sudip Nag and Maitree Bhattacharyya: Software, visualization

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6. Kalipada Bankura: Software, visualization, Writing-review and Editing, Formal analysis

7. Dipankar Mishra: Supervision, Writing-review and Editing, Funding Acquisition, Investigation, Software, visualization, Formal analysis

Appendix A. Supplementary material

CCDC number 1954538 contains the supplementary crystallographic data (excluding structure factors) in CIF format for the structure reported of complex. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

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GRAPHICAL ABSTRACT

